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ZnO NANOPARTICLE SYNTHESIS USING ND: YAG LASER FOR INCREASING HYDROGEN FUEL CELL PERFORMANCE

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ABSTRACT

In this work, the hydrogen evolution reactions on stainless steel electrodes in ultra-pure water (UPW) and water-based Zinc oxide colloid solutions have been investigated. Ultra-pure water with electrical conductivity (0.45µs) was used to synthesize ZnOnano colloidal using pulsed laser ablation of zinc metal in water. All experiments were performed using a Q-switched Nd-YAG laser operating at fundamental mode 1064nm with 9ns pulse duration, at fixed laser output energy (750mJ). Different number of pulses (250, 500, 750 and 1000) was applied with the aim to affect the concentration of synthesized ZnO colloidal. AFM micrograph of nano-colloidal was revealed that the synthesized nanoparticles have a spherical shape with average diameters about25nm. The pH and electrical conductivity values of all solutions were measured simultaneously at room temperature. Hydrogen generator-fuel cell driven by 30 volts as input source is developed with ZnO nanocolloidal. PH variation is within range 7-8.1 and electrical conductivity variation is 0.45-15.8 µs/cm. The optimum ZnO NPs concentration of pH 8.1 and electrical conductivity 15.8µs/cm has been observed, which gives the maximum H_2/O_2 output of 1.2 mL/s.

KEYWORDS: *Laser Ablation, ZnO Nano-Colloidal, Electrolysis & Hydrogen Generation*

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A Case Study

1. INTRODUCTION

The chemical and physical properties of materials at nano levels differ greatly when compared to micro levels. These properties show big differences in physical and chemical properties from the bulk material of which they are made [1]. Ultra small metal NPs with a high surface-to-volume ratio and “clean” surface, and hence a high density of active sites exposed to reactants, are significant for heterogeneous catalysis [2]. Preparing metal, metal oxide nanoparticles in a simple technique may be made using Pulsed Laser Ablation in liquid environments (PLAL). This technique has a good advantages compared with other physical and chemical methods like purity, the stability of the fabricated nano particle colloids, simple chemical preparation and do not require a vacuum chamber. Because of its ability to control NPs size by optimizing the laser parameter, making it the most flexible and promising technique [3].

Hydrogen has been well recognized as one of the most promising alternatives energy resources due to it’s a large specific energy capacity (120 kJ g $^{-1}$) and eco friendly emissions during combustion [4]. However, efficient and secure hydrogen production remains under considerable progress and ever expanding [5]. Water splitting driven by electrical or solar has gained great interest since one half reactions enable the production of

hydrogen. As most technologies breakthroughs were achieved through the development new functional materials, the choice of electrode or electrolyte besides variation of other conditions at the electrode and solution interface can reduce the energy level barrier and thus give a good reaction efficiency performance for hydrogen evolution reactions due to the different mechanism dominating in the given system. The electro-catalyst plays a vital role in the hydrogen evolution reaction (HER), since it can reduce the energy level barrier and thus give optimum reaction efficiency. Platinum (Pt) is the most widely used material as electrocatalytic and photocatalytic through the hydrogen-evolution reaction (HER). Even though Pt is highly active and stable under the often harsh operational conditions but the scarcity and high cost of Pt greatly hinder its large-scale applications [6]. Furthermore, developing lowered cost electrocatalysts, which possess comparable or even better catalytic activitythan Pt, led to having a way to solve these problems is to make a Pt alloy with a 3rd transition metal such as cobalt, nickel, iron and Iron Phosphide Nanoparticles[7,8].

On the other hand, ZnO nanoparticles synthesized by solution method have been studied for visible light-assisted photo-catalytic hydrogen generation besides other applications for photodetection, solar cell application and sensing [9, 10]. In this work, Laser ablation in a liquid medium has been adopted to synthesized ZnO nanoparticles. Their electrochemical performance has been studied and compared with ultra-pure water using electrical hydrogen generator.

2. MATERIALS AND METHODS

ZnO nanoparticles were produced by laser ablation of a Zn plate ($1\times1cm^2$), 99.9%) placed on the bottom of a glass vessel filled with 30 mL of UPW. The Zn target was irradiated directly by a Q-switched Nd-YAG laser (λ = 1064nm, pulse duration 9 ns) operated at 5 Hz. The vessel was continuously rotated to minimize the target etching effect, for production homogenous nanoparticles. The energy of laser pulses is750mJ. A different number of pulses (250, 500, 750 and 1000) were applied, to provide four solutions with different concentrations of ZnO NPs. The pH and electrical conductivity measurements for synthesized samples were performed using a Jenway Model 3505 pH meter and Crison Model EC- meter BASIC 30+ Respectively. ZnO particle size and surface roughness were determined from AFM (Atomic force microscopy).

Hydrogen generator consists of a glass container has12 stainless steel plates (10cm $\times$ 7cm $\times$ 0.1cm)as electrodes, is filled firstly with UPW driven by a direct current voltage equal to 30 volts, then the hydrogen generator is filled with prepared samples of ZnO NPS at different concentration each time. When the cell starts operating, the water is separated into hydrogen and oxygen and the produced gas is directed into a second graded glass tube, accumulated hydrogen volume was estimated by the water displacement method.

3. RESULTS AND DISCUSSIONS

3.1 Liquid-Phase Laser Ablation of Zinc Target

According to previous studies [11, 12], both physical and chemical reactions happened simultaneously during liquid-phase laser ablation (LPLA) will control the formation of ZnO nanostructures. Physical interaction initiates when a laser beam falls on a metal surface; absorbed energy from the laser pulse is converted into heat, a small amount of the sample will melt and evaporate to create a dense plasma above the metal interface[13]. This dense plasma expands at high velocity until the plasma extinguished and zinc clusters are formed. Consequently, the zinc clusters formed from plasma react chemically with the surrounding water medium to form zinc hydroxide, $Zn(OH)_2$, the latter will further decompose to form ZnO nanoparticles. The chemical equations described the formation of ZnO are given by Equations. 1 and 2

respectively [14]:

$$Zn + 2H_2O \xrightarrow{yields} Zn(OH)_2 + H_2 \tag{1}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{2}$$

The presence of ZnO nanoparticles in ultra-pure water was justified by both the carter creates at the target surface and the color change of the solution right after the laser ablation. Nanoparticle size and concentration, will lead to variation in the color of zinc oxide nanoparticle solution in water [15]. As shown in Figure 1the color of solution turns gray right after the laser ablation, depending on the number of pulses color became darker. The color variation is due to the high temperature and pressure released from the plume producing ZnO nanoparticles due to high kinetic energy of the laser beam onto the metal surface [16]. The solution in the beaker is warm when touched right after the laser ablation indicating the occurrence of the liquid-phase laser ablation mechanism. This experimental observation is in agreement with other studies [17].

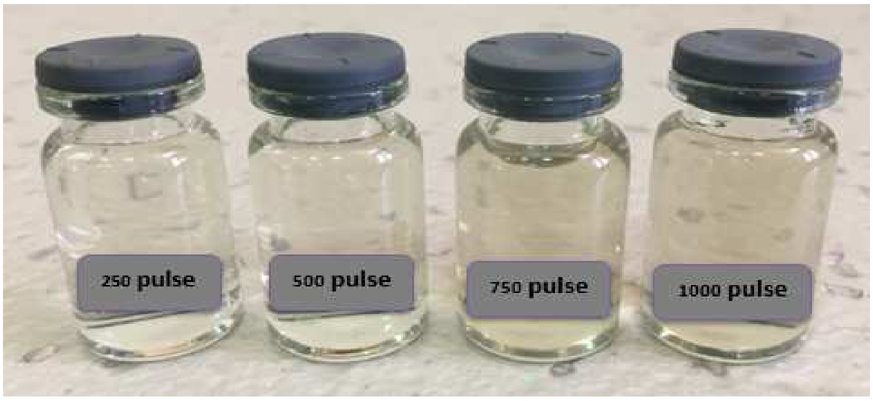


Figure 1: ZnO Nanoparticles Samples in Distilled Water

3.2 Atomic Force Microscopy (AFM) Analysis and Specific Surface Area (SSA)

The surface topography of ZnO thin film processed at fixed laser parameters was studied by AFM in contact mode. Figure 2 demonstrates 3D AFM image (8.17µm×8.17µm) of the ZnO nanoparticles films. From AFM image, it is seen that the ZnO surface is not smooth and the surface morphologies of the ZnO nanoparticles confirms spherical morphology. The surface roughness mean square (RMS) of the film is 5.71 nm. As material intrinsic property, specific surface area *SSA*(surface area per mass) has a special importance in the case of adsorption, heterogeneous catalysis and on surface reactions. This scientific value can be determined from Eqs. 3 and 4:

$$SSA = \frac{SA_{particle}}{\rho . V_{particle}} \tag{3}$$

Where $V_{particle}$ is particle volume and $SA_{particle}$ is particle surface area[18].

$$SSA = 6 * 10^3/(\rho . D_p) \tag{4}$$

D_P is the size of the particles and ρ is the density of bulk zinc oxide 5.606 g/cm^3. Both of these correlations give the same result. An estimated value of *SSA* of the prepared ZnO nanoparticles was (42.8m^2/g) corresponding to an average primary particle diameter of 25 nm.

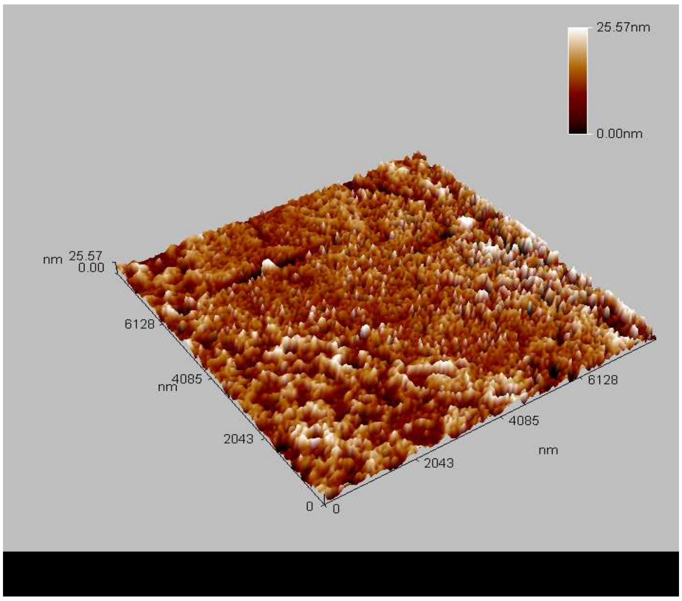


Figure 2: AFM Micrograph of Synthesized ZnO Nanoparticles

Generally, fabrication of nanoparticles using PLAL depends on laser parameters, target materials, the optical path of a laser beam and the nature of liquids. The formula for in ultrafast laser processing based on the two-temperature model described laser-mater interaction [19]. Based on this work ablated mass (*m*) can be calculated from Eq. 5:

$$m = N.\rho.A.\alpha^{-1}.ln\frac{Fa}{F_{th}} \qquad (5)$$

where N is the number of laser pulses, □ is the density, A the focal spot area, α^{-1} the optical penetration depth, F_a the laser fluency and F_{th} threshold fluency for ablation. Considering other parameters are constant, an increase in a number of pulses(ablation time) will lead to an increase the ablated mass and then the concentration of nanoparticles. Synthesis of more nanoparticles in a liquid environment at higher ablation times was previously reported [20].

3.3 pH and EC Measurements of Nano-Colloidal

Figure 3illustrate the evolution of pH value of synthesized samples as the function of the increasing pulse numbers. The starting pH value of the nanofluid sample was 7.9 with regard to the base fluid (Water), and then at the higher number of laser pulses, the rate of increase of pH values became lower or even saturated at approximately 8.1. In other words, the differences in pH value decrease as the ablation time increase. This behavior may be attributed to higher volume fraction achieved after laser ablation and dispersion of ZnO nanoparticles and this result agree with reference [21]. On the other hand, the electrical properties of the base fluid have changed after target ablation. The electrical conductivity of the UPW is measured to be 0.45µs/cm. Figure 4shows the electrical conductivity values of nano-colloidal with a different number of pulses. It is clear from the figure that E.C increased in a linear behavior as the number of pulses increased. The main reason for this trend is the dispersion of nanoparticles in the base fluid during laser ablation leading to significantly enhanced the volume ratio of (Water-ZnO nanoparticles system) which in turn leading to formation surface charges by polarization. Theoretical and experimental studies available in [22] reported that the polarization process at nanofluid is enhanced by the effective dielectric constants and the densities of both the nanoparticles and the base fluid.

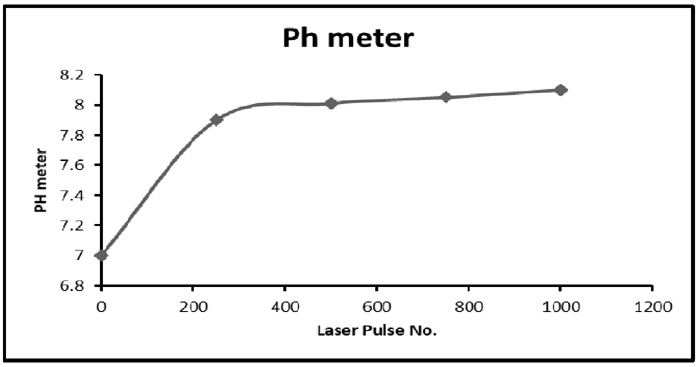


Figure 3: pH values of Synthesized Samples as a Function of Laser Pulses

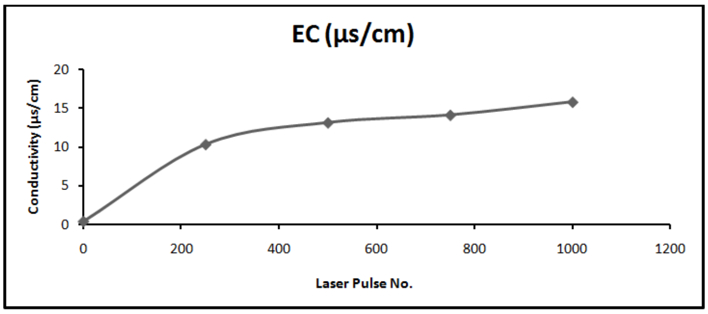


Figure 4: Electrical Conductivity of Synthesized Samples as a Function of Laser Pulses

3.4 Accumulated Gas Volume

Hydrogen generation experiments using ultra-pure water (UPW) and ZnO nanoparticles synthesized at different laser pulses ablation were carried out via electrochemical water splitting and accumulated gas was quantified using liquid displacement at room temperature. Figure 5 shows the accumulated gas volume by electro-splitting of pure water and with ZnO nanoparticles synthesized at the different number of pulses. It can be observed that all samples have clearly shown hydrogen evolution that increased linearly with respect to time. Amongst all samples, it was observed that higher rate of accumulated hydrogen generated is (380mL) for ZnO NPs concentration (1000 laser pulses) with pH 8.1 and electrical conductivity 15.8µs/cm, compared with water and other ZnO samples which may be due to its high concentration. The hydrogen generation rate was further increased by an increase of pH of the solution.

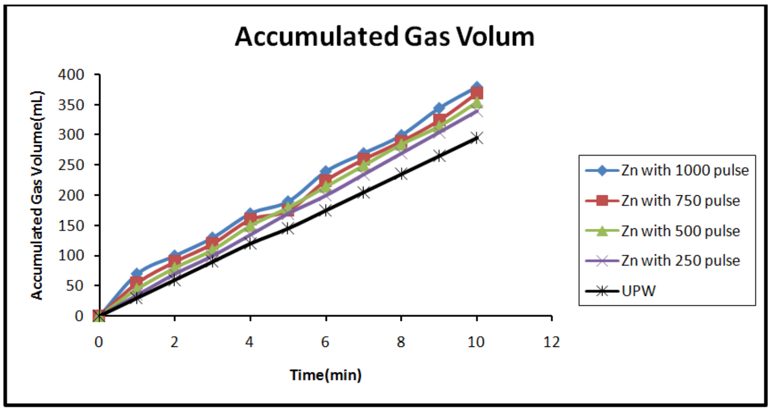


Figure 5: Accumulated Gas Volume as a Function of Time with Ultrapure Water and with ZnO Nanoparticles Synthesized at different Number of Pulses

To further investigate chemical reactions inside the cell, the electrical current of the cell has been measured as a function of accumulated gas volume and the reaction time. As shown in Figures 6 and 7, the current shows the same trend for all samples. There is an increase in current with increasing of time and the volume of accumulated gas.

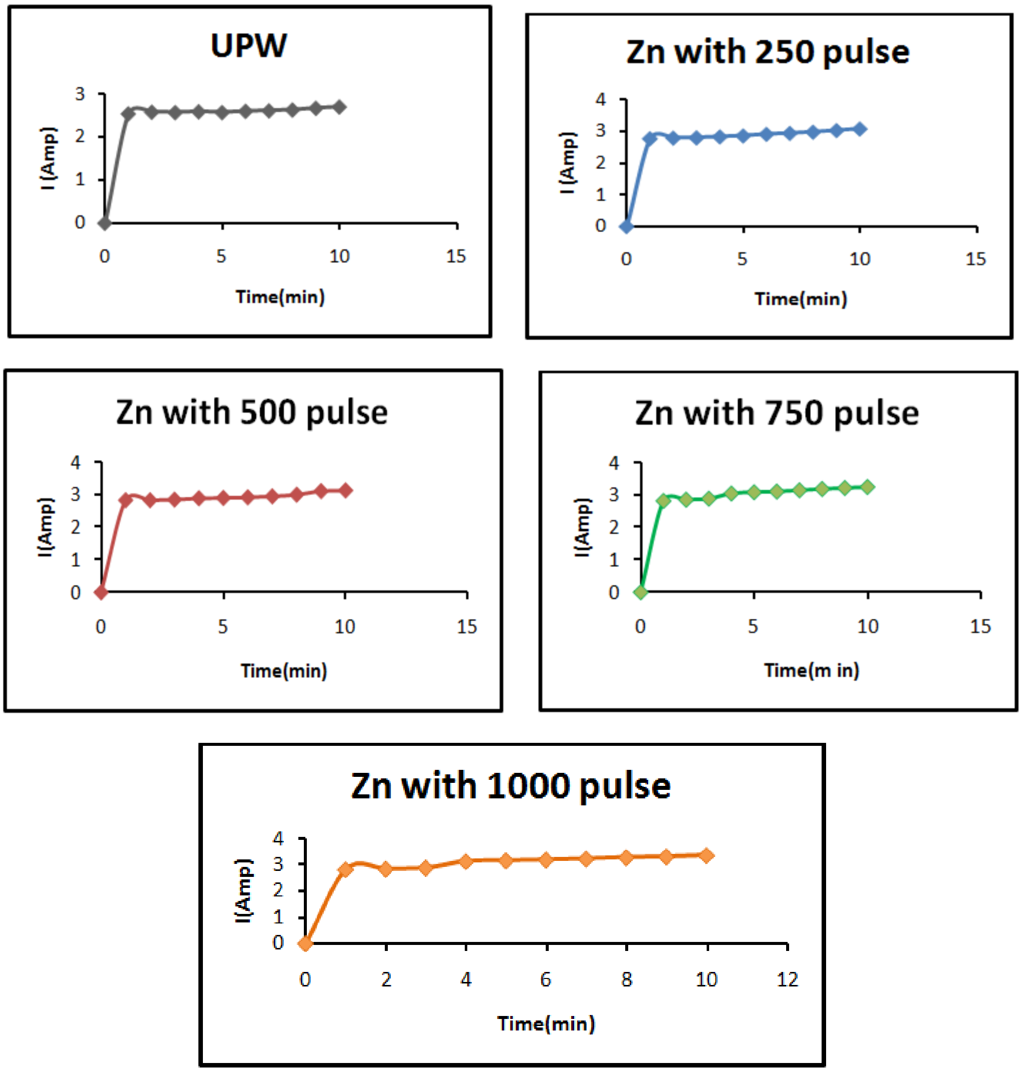
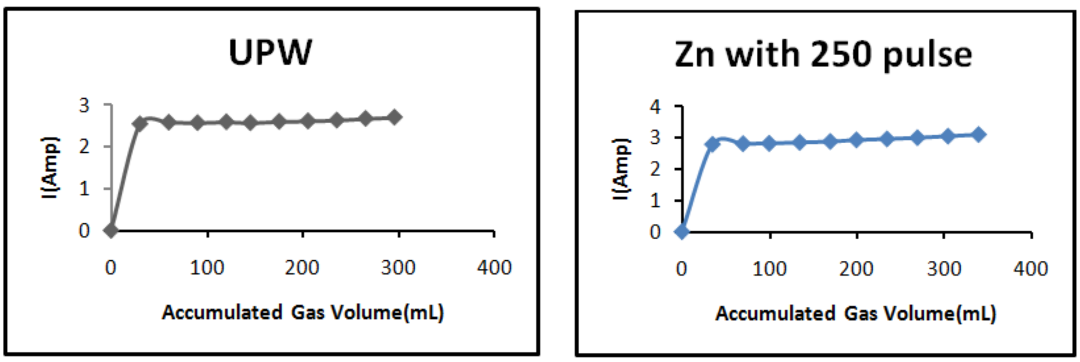


Figure 6: The Current Consumption as a Function of Time with Ultrapure Water and with ZnO Nanoparticles Synthesized at different Number of Pulses



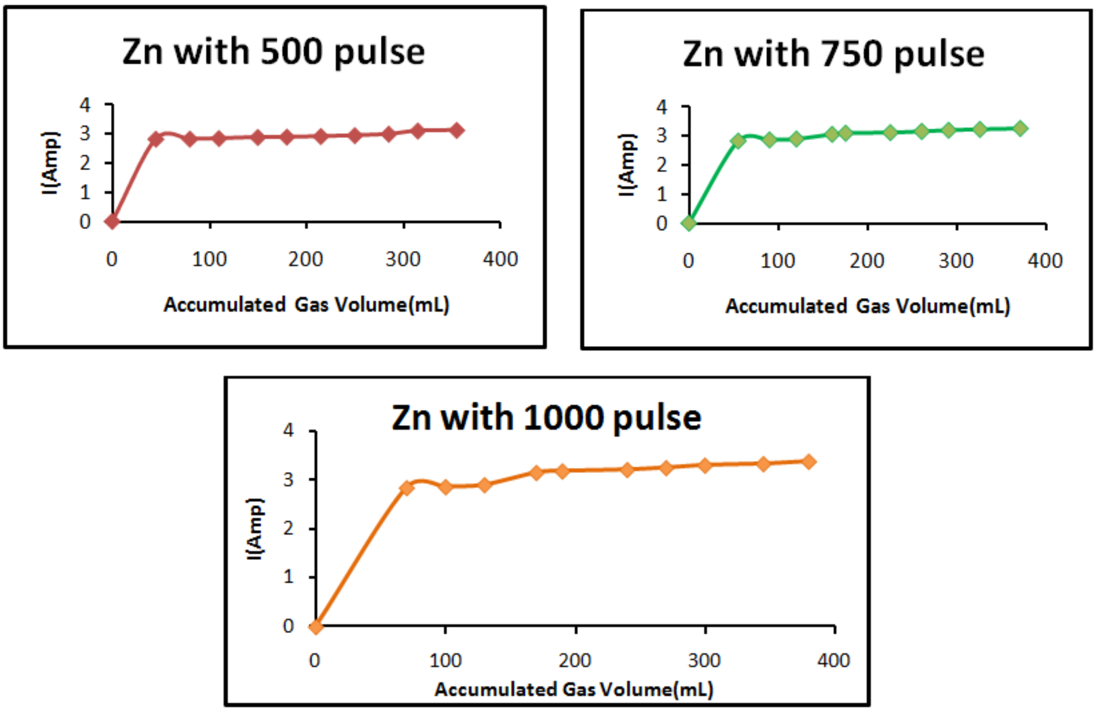


Figure 7: Accumulated Gas Volume as a Function of the Current with Ultrapure Water and with ZnO Nanoparticles Synthesized at different Number of Pulses

4. CONCLUSIONS

Zinc Oxide nanoparticles were synthesized by pulsed laser ablation of zinc target in ultra-pure water. The effect of laser number of pulses was studied using a 1064nm wavelength of an Nd:YAG laser with an exerted energy of 750 mJ/Pulse. Majority of nanoparticles in all samples areabout25 nm as depicted in AFM micrograph. The results indicate that higher number of laser pulses produce a higher concentration of dispersed nanoparticles which play a crucial role that influences the effective of increasing pH and electrical conductivity of nanocolloidal suspension, this suspension is used as an electrolyte in the hydrogen generator, which led to increment in the hydrogen accumulated gas production. Electrochemical results confirm an overall enhancement of hydrogen evolution reaction with ZnO nanoparticles.

NOMENCLATURE

A focal spot area, cm^2

D_p size of the particles, nm

F_a laser fluency, J/cm^2

F_{th} threshold fluency for ablation, J/cm^2

N number of laser pulses

$V_{particle}$ particle volume, cm^3

$SA_{particle}$ particle surface area, cm^2

GREEK SYMBOLS

ρdensity of bulk zinc oxide, g/cm^3

α^{-1}optical penetration depth

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